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Progress in thermal plasma deposition of alloys and ceramic fine particles

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Abstract - The recent progress of thermal plasma processes for deposition of fine powder of various metallic and ceramic materials is outlined in this report. R.F. plasma processes for synthesis of ultra fine powder (UFP) of non-oxide ceramic materials such as silicon nitride and silicon carbide are mainly described. Plasma evaporation processes for production of metallic UFP and R.F. plasma processes for synthesis of ceramic UFP which have been developed lately in Japan are explained in detail. The importance of a national research project to be started in order to develop plasma materials processing in this year in Japan is also simply described.

INTRODUCTION

It is very difficult to produce metallic or ceramic fine powder of diameter less than 1000 nm by using spraying techniques with compressed inert gas or liqiud and mechanical means such as crushing and grinding.

Lately developmental researches for a large scale production of ultra fine powder (UFP) of metals and ceramic materials are being actively carried out in Japan. UFP of various metals of diameter less than 100 nm can be formed by evaporation and condensation of the metals at reduced pressure in the region of 0.5-50 torr in an inert gas such as Ar. Uyeda and Kimoto (ref. 1) have published such simple method in 1963. This method has been developed in Japan and UFP of several kinds of metals is being produced by melting and evaporation of the metals by R.F. induction heating in a small plant scale. UFP of most of alloys and ceramic materials cannot be easily produced by such method, considering the formation mechanism of UFP during cooling and condensation of metal vapor. A method of UFP production using thermal plasma for evaporation of metals is called "Plasma Evaporation Process". In this case, generally a molten metal pool under high intensity plasma arc is used as an an evaporation source of metal, while there is another method in which small particles of metals are injected into thermal plasma and evaporated by heat transfer to the particles from the plasma. When a reactive gas such as nitrogen or methane is mixed into plasma forming gas, UFP of nitride or carbide of evaporated metal can be synthesized by thermal gas phase reaction and rapid cooling of the product. This method is called "Reactive Plasma Evaporation Process". In so-called "Thermal Plasma CVD", a mixture of gaseous reactants are introduced into inert gas plasma for preparation of metallic and ceramic UFP and in some cases the reactants serve as plasma forming gases simultaneously. "Thermal Plasma CVD" seems to be most suitable for synthesis of ceramic UFP.

The recent progress of the above mentioned plasma processes for preparation of UFP is outlined, laying stress on R.F. plasma processes for synthesis of UFP of non-oxide ceramic compounds in this paper.

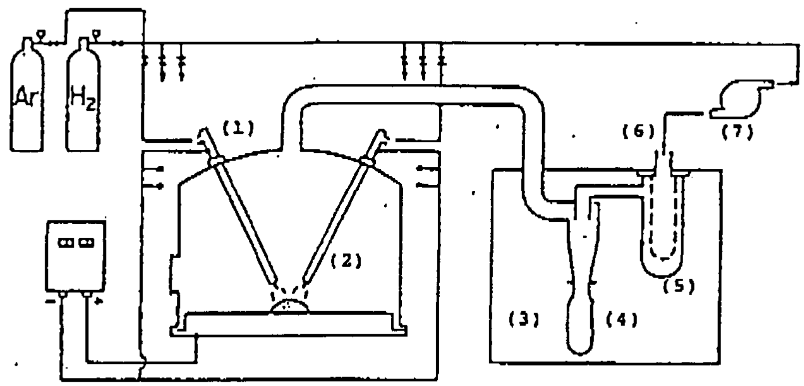
PLASMA EVAPORATION PROCESS

A. EVAPORATION OF MOLTEN METAL POOL

The evaporation and condensation process of anode material overheated under a transferred plasma arc was used for the first time for preparation of UFP of the anode material in 1952 (ref. 2). UFP of many kinds of metals, oxides and carbides was formed by this evaporation process using transferred argon plasma arc. In these both cases, it must be emphasized that a large potential drop at the anode promotes energy transfer of the arc to the anode

material and its vaporization. Horizontally rotating d.c. plasma furnaces have been developed for heating and vaporizing a ceramic material consisting of inside wall of the furnace (ref.3, ref. 4). UFP of the ceramic material are condensed from its vapor at an outlet of the furnace by gas quenching.

A new process for production of UFP of various metals by using d.c. hydrogen plasma arc has been developed recently at National Research Institute for Metals in Japan (ref. 5). A schematic diagram of the apparatus is shown in Fig. 1.



(1):Gas Inlet, (2):Tungsten Electrodes, (3):Globe Box, (4):Cyclon
(5):Filter, (6):Gas Outlet, (7):Gas Circulation Pump

Fig. 1. A schematic diagram of an apparatus using plasma arc for production of metallic UFP developed by Ohno and Uda (ref. 5)

In this process, some drastic changes of phisical and chemical properties of hydrogen contacting molten metal at very high temperatures under plasma arc are utilized effectively. The plasma arc between six tungsten electrodes (cathodes) and a massive metal on a copper hearth (anode) is generated under atmospheric pressure in a steady flow of H_2-Ar mixture (H_2 : 30-70%). Metallic UFP can be efficiently formed by a kind of forced evaporation of molten metal superheated due to the increase of heat transfer from argon-hydrogen plasma arc including a large amount of atomic hydrogen. Such UFP formation can be also promoted by the phenomena that a dissolution rate of hydrogen in a superheated part of molten metal just under the plasma arc is very high and a release rate of hydrogen from non-superheated metal at the circumference of plasma arc root increases remarkably comparing with that from the superheated part. UFP is carried with gas flow into a collector consisted of a cyclon and a cylindrical filter paper. The diameter of UFP produced by this process is in the range of 50 nm ~ 5000 nm, but 20 nm ~ 100 nm in some cases. In the case of iron UFP, its production rate (= amount of evaporation per unit area and unit time)is about 3 times as much as that in usual evaporation processes. A typical experimental condition in this process is shown in Table 1.

Table 1. A typical experimental condition in Ar-H_2 plasma evaporation process (ref. 6)

Atmosphere	50%H_2- Ar
Pressure	101325 Pa
Gas flow rate	$5\times10^{-4} m^3/s$
Arc current.	260 A
Arc voltage	22-25 V
Reaction time	15-540 s
Sample volume	$3\times10^{-6} m^3$

It has been reported that fine spherical iron particles can be obtained by plasma arc evaporation process under nitrogen atmosphere at reduced pressures (~1000Pa), but in this case the nitrogen content in these particles was very high. In view of the present consequence, the productivity of metallic UFP in the above-mentioned hydrogen plasma evaporation process is better than that in other metallic UFP production processes.

B. EVAPORATION OF SMALL PARTICLES OF METALS

Sheer et al (ref. 7, ref. 8) has reported that UFP of several kinds of oxides produced by evaporation of small solid particles of the oxides injected into a d.c. Ar plasma arc. In this case it is very interesting that an electromagnetic pumping effect arising around a d.c. arc cathode facilitates the introduction of small oxide particles into the plasma arc column.

R.F. plasma evaporation process is also used for metallic UFP fprmation from small particles of the metal. The possibility of UFP formation of alloy from small particles of its metal components introduced in R.F. Ar plasma under atmospheric pressure was suggested by Gal' (ref. 9). Alpha phase iron or metastable gamma phase iron including a small amount of alminum was obtained by evaporation of the mixture of iron and aluminum powder in plasma. It was estimated that the quenching velocity by gas injection was 10^4-10^5 K/s in this experiment.

Three types of R.F. plasma torches as shown in Fig. 2 are used for UFP synthesis of alloys and ceramic materials in our laboratory.

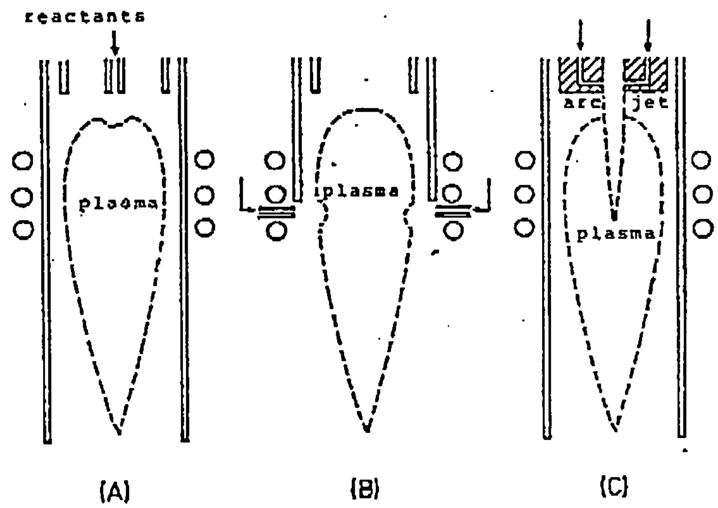


Fig. 2. Schematic drawing of three types of R.F. plasma torches

The type (A) torch (conventional torch) has been used in most of R.F. plasma processes since pioneering works by Reed (ref. 10, ref. 11). In this type (A) torch, the stability of plasma flame is apt to be disturbed with injection of reactants. Therefore reactants are often introduced into the tail flame of plasma, however in most cases the low percentage recovery of products is obtained. In the type (B) torch, reactants are injected into a fire ball zone of plasma flame at the position of R.F. coil for the both purposes of higher percentage recovery of products and stabilization of plasma. In the type (C) torch, a very stable plasma flame can be generated in an R.F. plasma torch in combination with a d.c. plasma jet torch. This type one is often called "hybrid plasma torch" in Japan.

UFP of Nb-Al and Nb-Si alloys has been synthesized by evaporation process of mixed particles of Nb and Al/Si introduced into an R.F. plasma reactor provided with the type (B) plasma torch (ref.12), but it was impossible to control the composition UFP containing Nb and Al. The outline of this reactor is shown in Fig. 3. UFP of V-Si alloy with a controlled and fixed composition has been synthesized from mixed particles of V and Si by using the same type reactor. The experimental condition and result are summarized in Table 2 (ref. 13).

Plasma modelling is very useful for the estimation of gas velocity distribution and temperature distribution in plasma flow and the analysis of the problems of heterogeneous heat and mass transfer (plasma-wall or plasma-particle). Fauchais et al have published a detailed review on excellent plasma models presented by a few researchers. It is very important to analyse the problems

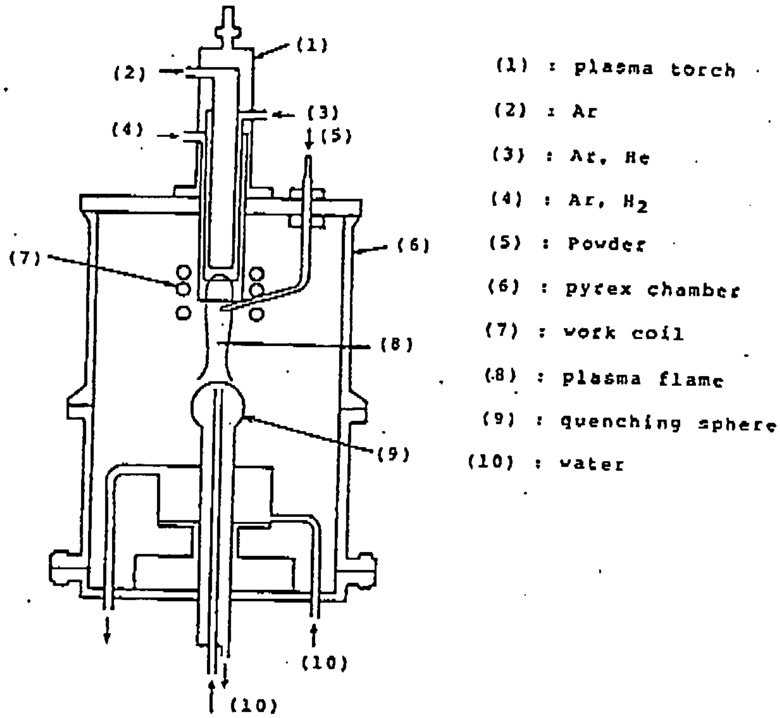


Fig. 3. Plasma flow reactor using type (b) torch (Fig. 1) designed for co-condensation process of high temperature metallic vapors.

Table 2. Experimental condition and phases of V-Si UFP detected by X-ray diffraction analysis

Gas flow rate
Plasma gas : 10 l/min(Ar) + 5 l/min(He)
Sheath gas : 40 l/min(Ar) + 4 l min(H_2)
Carrier Gas : 4 l/min(Ar)

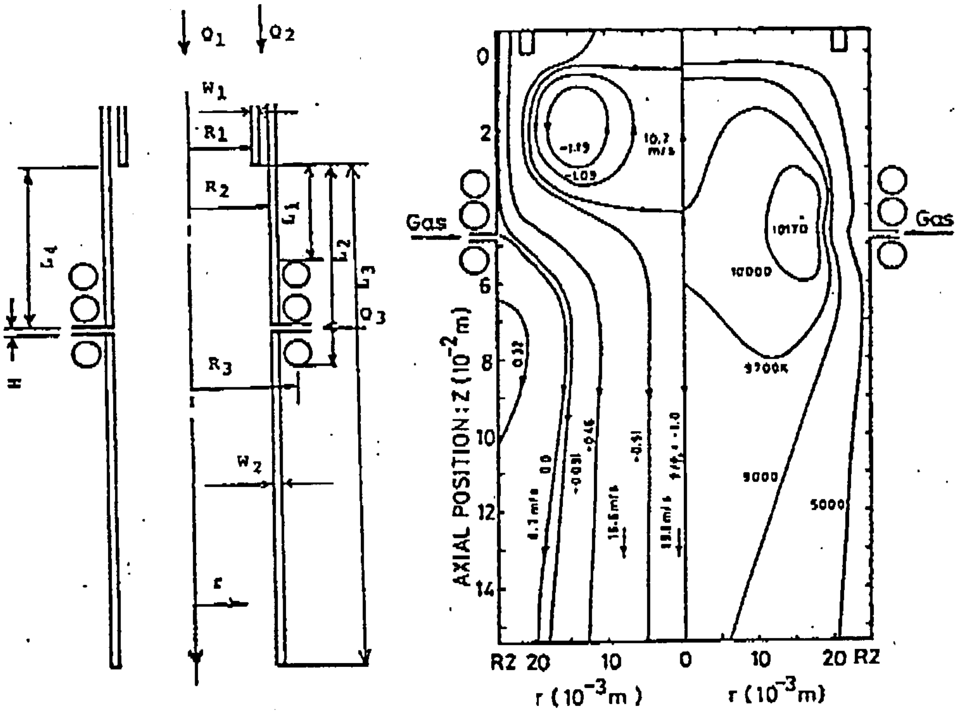
Plate power output : 35 kW

Coil current : 110 A

Powder feeding rate : 0.5 g/min

System	Composition of feed powder (at.% Si)	Detected phases	Equilibrium phases
V-Si	67	VSi_2	VSi_2
	40	V_5Si_3	V_5Si_3, VSi_2
	37.5	V_5Si_3	V_5Si_3
	35	V_5Si_3, V_3Si	V_5Si_3, V_3Si
	25	V_3Si	V_3Si

of plasma-particle heat transfer, particle velocity, particle temperature, and particle trajectries for explanation of the plasma evaporation mechanism of particles. An example of temperature and flow patterns of Ar plasma under atmospheric pressure estimated in the type (B) torch is shown in Fig. 4. The method for calculation here is basedon the model by Boulos (ref. 14), that is, the continuity, momentum, and energy equations are solved simultaneously with the electric field and magnatic field equations making use of the numericla procedure developed by Gosman et al (ref. 15). It can be concluded from this result that eddy flow pattern in the upper part of plasma is not disturbed by



R_1 : 20 mm, R_2 : 25 mm, R_3 : 30 mm, L_1 : 30 mm, L_2 : 60 mm, L_3 : 160 mm, L_4 : 48 mm, W_1 : 2 mm, W_2 : 2 mm, H : 1 mm, Q_1 : 10 l/min, Q_2 : 20 l/min, Q_3 : 9.5 l/min, Oscillator frequency : 4 MHz, R.F. coil current : 110 A, Ψ_o = 1.097 X 10^{-4} kg/sec

Fig. 4. Type (B) torch geometry, dimension, and an example of stream line patterns and temperature distribution in Ar plasmas. (ref. 16)

such gas injection through a narrow annular slit of the torch at the lower end of R.F. coil and the stability of plasma can be sustained. An example of the temperature and flow patterns of Ar plasma under atmospheric pressure in the type (C) torch is shown in Fig. 5 (ref. 17). The effect of d.c. plasma jet remains, to some extent, in these patterns.

The nucleation and growth mechanisms of metallic UFP in R.F. Ar plasma tail flame at atmospheric pressure have been discussed in detail by Yoshida and Akashi (ref. 17) and Harada et al (ref. 12). It has been made clear that the growth of UFP occurs at higher temperature in the plasma tail flame than in the inert gas atmosphere in the gas evaporation process at reduced pressures described in INTRODUCTION of this paper, and that the growth of UFP must be under the control of collision and coalescence of particles (clusters) in fog state (so-called "Collision and Coalescence Model"). For example, the relation between number and diameter of each particle included in iron UFP produced by our plasma evaporation process obeys the log-normal distribution function (Gaussian distribution) (ref. 17). This fact supports that collision and coalescence model gives an explanation of UFP formation mechanism in plasma tail flame, as pointed out by Granqvist and Buhrman (ref. 18). The nucleation temperatures of Nb, Si, and Al from those vapor can be estimated by "Rothe-Pound Theory" considering rotation and transition motions of cluster of these elements (ref. 12). From such consideration, it has been deduced that the formation of UFP of Nb-Al or Nb-Si alloy is possible only in the case controlled by collisison and coalescence mechanism of clusters in fog state. The calculated value of average diameter of UFP is about 10 nm which is in close agreement with its determined value experimentally.

In conclusion, plasma evaporation process using powder as raw material is very suitable for synththesis of UFP of alloys, if very large cooling velocity of vapor of alloy's components can be attained by newer quenching techniques. But the low productivity of UFP in this process is a problem.